CHAPTER 15

Data Review Reports

15-1. Introduction.

a. In general, second column confirmation is required for chromatographic methods with 2-D detectors when the analytes of concern have not been well characterized. For single-component (i.e., single-response) analytes, a "tentative" identification of a target analyte occurs when the peak associated with the analyte falls within the retention window for the "primary" column. A "confirmed" identification occurs when the analyte peak also falls within the retention time window for "secondary" or "confirmatory" column. The confirmatory and primary columns must be dissimilar columns (i.e., must possess different stationary phases) so that the elution order for the target analytes reported from the primary and secondary columns differ. Target analyte identification for multi component (i.e., multi response) analytes (e.g., Aroclors by GC) are primary performed using pattern recognition. Hence, second column confirmation would typically be performed only if the identity of the analyte were in doubt (e.g., would be performed for weathered Aroclors by GC).

b. A quantitative result from the "primary" column and a confirmed identification from the "confirmatory" column are minimally required for second-column confirmation. In other words, if the "primary" column possesses quantitative capability, only detection capability is minimally required for the "confirmatory" column. However, it is usually desirable to apply the same QC criteria to both the "primary" and "confirmatory" columns and to report quantitative results from both analytical columns. (Note, that under these circumstances, the column designations "primary" and "confirmatory" are arbitrary; results reported from either column are equally reliable.) This strategy is advantageous because it provides a measure of instrument duplicate precision. In addition, when a chromatographic interference occurs for the primary column but does not prevent confirmation, a quantitatively reliable detection may still be reported from the confirmatory column.

15-2. Criteria.

15-2.1. Frequency.

Unless the analytes of concern have been well characterized or confirmation will be performed using an instrument with a 3-D detector, second column confirmation must be performed for all detections (i.e., all results above the reporting limits).

15-2.2. Duplicate Precision.

Unless otherwise specified, assume that quantitative results must be reported from both the primary and confirmatory columns. If a target analyte is detected with both the primary and confirmatory column and the result reported from one (or both) of the columns is greater than the quantitation limit, then the RPD calculated for the pair of results must be less than or equal to the absolute value of twice the uncertainty tolerance for the CCVs. In particular, if the error toler-

ance for the CCV is ± 20% (e.g., 80% - 120%), then the RPD must be within 40% (2 × 20%). The RPD for each pair of results is calculated from the equation:

$$\text{RPD} = 100 \, | y_1 - y_2 | \, / \, [(y_1 + y_2) / 2]$$

where y_1 and y_2 denote the results from the primary and secondary columns.

15-3. Evaluation.

Verify that all single component analyte detections were confirmed. Confirmation for multi component analytes will be dependent upon the nature of the contamination and the objectives of the investigation. All results above the reporting limit must fall within the retention time windows for both analytical columns. If possible, verify that dissimilar chromatographic columns were used for the primary and confirmatory columns. Calculate the RPD for a pair of results and ensure that the calculated and reported values agree to within two significant figures.

15-4. Qualification.

a. The qualification strategies must distinguish *quantitative* reliability from *qualitative* reliability. *If second-column confirmation is required for the project but was not performed, then, at a minimum, qualify all single-component analyte detections with the N flag (the results are not qualitatively reliable).* Based upon the objectives of the project, the X or R flag may be more appropriate. *If the nature of the site contamination has not been well characterized, then qualify all the detections with the X or XN flag.* For example, if PAH analyses, by liquid chromatography with a UV detector, are being performed for a new study area for a risk assessment and some valid confirmation procedure was not performed, then it would probably be appropriate to qualify detections (especially low-level detections) as tentatively rejected. The X flag should be used when detections are greater than project-specific action levels and a conservative estimate is inappropriate (for the particular phase of the project). However, note that, if a sample is analyzed using second-column confirmation, but an analyte is not confirmed in the sense that the analyte peak is detected with the primary column but not with the confirmatory column, then the analyte result is reported as “not detected” (e.g., using the U flag).

b. At a minimum, qualify all detections with the N flag, if, in the reviewer’s professional judgment, the two analytical columns are not sufficiently dissimilar (e.g., a C-18 column is used with a C-8 column instead of a CN column for explosives by HPLC).

c. Chromatographic interferences from coelutions can affect the quantitative as well as the qualitative reliability of the data. A high (i.e., noncompliant) RPD may result because one or more non-analyte peaks that elute in the retention time window for the analyte of interest. Qualify the results with high RPDs as follows:

(1) If the RPD is unacceptable high, at least one of the results is above the method quantitation limit, and the chromatograms are not available for review, or a coelution cannot otherwise be definitively identified, then, at a minimum, qualify the results from both the primary and confirmatory columns as qualitatively and quantitatively estimated using the NJ flag. Qual-

ify the results with the X flag when a gross failure occurs and the reason for the unacceptable RPD is not apparent. However, if a decision level is available and both results are less than the decision level, then NJ flag may be more appropriate. It is recommended that a gross failure be defined to occur when the calculated RPD is greater than two times the RPD acceptance limit (e.g., when the RPD > 80%).

(2) If the result from the primary column and the corresponding result from the secondary column are both less than the quantitation limit and a high RPD is obtained, then qualify both results with the J flag (rather than with the N flag).

(3) If it can be determined that a high RPD value arises from a coelution problem but confirmation is unaffected, then only qualify the result from the column with the coelution problem as quantitatively estimated or rejected. For example, assume that detections greater than the quantitation limit for a particular target analyte are reported from both the primary and confirmatory columns, but the result from the primary column is not quantitatively reliable because a non-target analyte gives rise to a very large broad shoulder on the target analyte peak. Since confirmation is unaffected and a quantitative result is available from the confirmatory column, the result from the confirmatory column would be reported as unqualified (assuming that all other QC criteria are met), but the result from the primary column may be rejected for quantitative reliability. However, it should be noted that a comprehensive data package would typically be required to perform this type of evaluation.

Table 15-1
Qualification for Second-Column Confirmation [1]

RPD	Result	Reported (Qualified) Result
RPD < 40%	MRL < MQL < y_1 MRL < MQL < y_2	y_1
	MRL < y_1 < MQL MRL < y_2 < MQL	y_1 J
RPD not calculated because y_2 < MRL	y_1 > MRL	MRL U
40% < RPD < 80%	MRL < MQL < y_1 MRL < MQL < y_2 $y_2 > y_1$	y_1 NJ and y_2 NJ [2] or y_2 NJ
	MRL < y_1 < MQL MRL < y_2 < MQL	y_1 J
RPD > 80%	MRL < MQL < y_1 MRL < MQL < y_2 $y_2 > y_1$	y_1 X and y_2 X If y_1, y_2 < AL, then y_1 NJ and y_2 NJ
	MRL < y_1 < MQL MRL < y_2 < MQL	y_1 J
RPD not calculated because confirmation was not performed	MRL < MQL < y_1	y_1 N or y_1 X
	MRL < y_1 < MQL	y_1 JN or y_1 X
	y_1 < MRL	MRL U

Notes: 1. Assume both columns are acceptably calibrated and all QC samples are in control (with the possible exception of the RPD). The result, y_1, is being reported from the primary column and result from the confirmatory column is denoted by y_2. The acceptance limit for the RPD is assumed to be 40%. 2. When the RPD > 40 and the reason for the high RPD is unknown, then the preferred approach is to report the results from both columns. As per the USEPA OSW memorandum "Clarification Regarding Use of SW-846 Methods" of 7 August 1998, "an approach that is conservative relative to environmental protection is to report the higher of the two values when the relative percent difference is greater than 40% *and* no interferences or chromatographic anomalies are evident." However, if it can be determined that the high RPD is from a chromatographic interference for one of the columns, then report the result from the remaining column (unqualified).